A brief history of light microscopy applied to Portland cement clinker

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Abstract

The application of microscopic methods to raw materials, clinker, cement and hydrated cementitious systems has contributed significantly to the understanding of the chemical and mineralogical composition of clinker, its formation conditions and hydration reactions over the last 140 years. This publication reviews the contributions of important microscopists, the development of the method and the main issues addressed by light microscopy applied to Portland cement clinker.

Keywords *clinker, light microscopy, history, thin sections, polished sections*

Introduction

Portland cement clinker is still, 200 years after Joseph Aspdin's patent for what he called "Portland cement" and 180 years after his son William probably produced the first "modern" Portland cement, the essential constituent of most cements today. After these inventions, which were probably based more on luck than on chemical understanding, generations of scientists from different disciplines built up the field of cement chemistry. A number of significant contributions to the understanding of the chemical and mineralogical composition of clinker, its formation conditions and hydration reactions have been made by the application of microscopic methods to raw materials, clinker, cement and hydrated cementitious systems (hardened cement paste, mortar, concrete).

This publication reviews the contributions of important microscopists, the development of the method and the main issues addressed by light microscopy applied to Portland cement clinker. Various aspects have been described in many articles and textbooks, in many languages, published over many decades. Due to language barriers and the limited availability of primary literature, much of the work on this subject has probably remained unknown to the author and is therefore missing.

Pioneers

It is difficult to pinpoint the very first documented application of optical microscopy to cementitious materials. Two of the earliest mentions are by Anton Hopfgartner [1] and Max Pettenkofer [2], both from 1848 and both referring to the same analysis by Hopfgartner in von Pettenkofer's laboratory. However, only cement particle shapes were described here. In 1880, Ludwig Erdmenger described observations on Portland cement powder and on thin sections of hardened Portland cement [3], but also without any significant insight into phase composition or hydration mechanisms.

The first researchers to significantly improve our understanding of clinker using microscopy were the French chemist Henry Le Chatelier and the Swedish geologist Alfred Elis Törnebohm. Both used a polarising microscope on thin sections of clinker. Le Chatelier first published his findings in an article in 1882 [4] and later in his thesis in 1887 [5; cf. 6]. His work included descriptions of the shapes, birefringence and colour of the phases he had observed, as well as the first drawings of clinker sections under the microscope (Fig. 1).

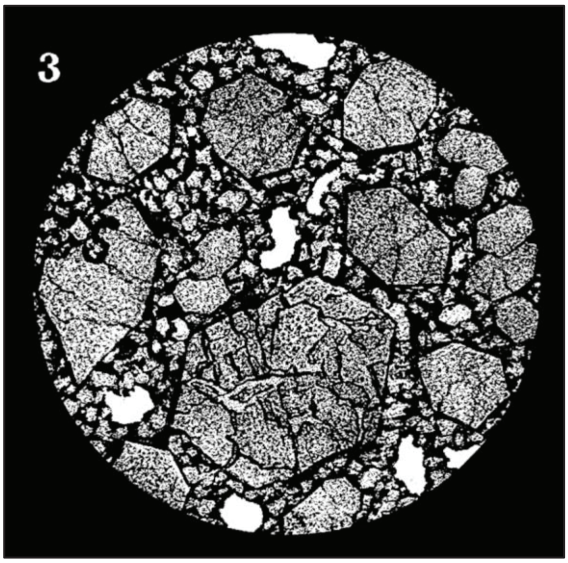

Figure 1 *Hand drawing of microscopic view on a thin section of clinker; from [5], original width: ca. 60 mm.*

Törnebohm presented his findings at a congress of the Association Internationale d'Essais des Matériaux (A.I.E.M., a predecessor of today's RILEM) in Stockholm in 1897. This contribution was published in German in the same year in a journal (without figures) [7] and in a booklet published by an association of Scandinavian Portland cement manufacturers [8]. The text included descriptions of the clinker phases observed by Törnebohm and he famously introduced the names alite, belite, celite and felite, the first two of which are still in use. The booklet also contained four coloured drawings of clinker sections (Fig. 2).

The main purpose of these first microscopic investigations was to clarify the so-called "constitution" of Portland cement clinker, i. e. to identify the mineral phases and their respective chemical compositions as well as their typical contents in clinker. For example, in 1904 H. Kappen used polarised light microscopy on thin sections of laboratory samples to confirm that belite is C_2S [9]. His publication again included drawings of microscopic observations (Fig. 3).

Figure 2 *Hand drawing of microscopic view on a thin section of clinker with phase indication; from [8], original width: ca. 90 mm.*

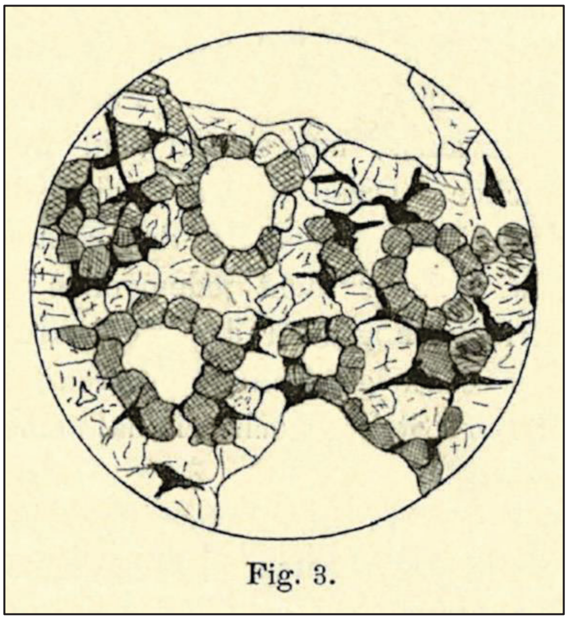

Figure 3 *Hand drawing of microscopic view on a thin section of laboratory clinker; from [9], original width: ca. 55 mm.*

Developments

Until the 1930s, polarised light microscopy on thin sections was the main method for clinker microscopy. While this technique provides the opportunity to observe several important phase properties such as colour and birefringence in addition to the microstructure, it has one important drawback: petrographic thin sections are typically 25 to 30 µm thick. In ordinary clinker, most of the crystals of the different phases have diameters below this. It is therefore the rule rather than the exception for several crystals to overlap making identification of small crystals and representative interpretation of the microstructure very difficult.

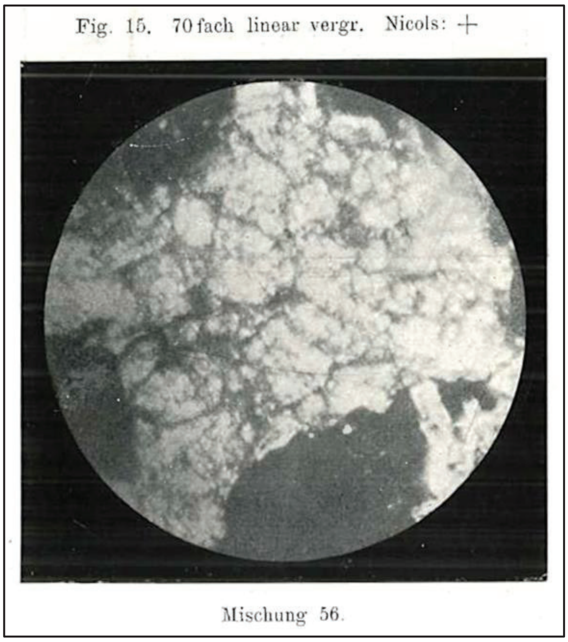

Figure 4 *Photomicrograph of a thin section of laboratory clinker; from [10], original width: ca. 80 mm.*

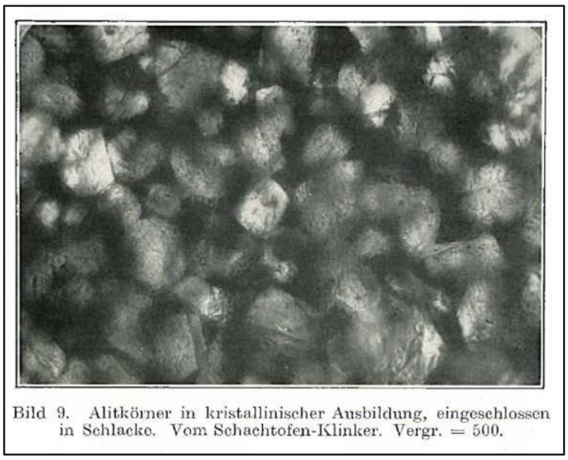

Figure 5 *Photomicrograph of a thin section of shaft kiln clinker; from [11], original width: ca. 100 mm.*

While this effect is not documented in the drawings of the early works, it is clearly visible in the photographs that replaced the drawings in later publications. Possibly the first black and white photomicrographs of clinker thin sections can be found in lectures by Jänecke [10] (Fig. 4) and von Glasenapp [11] (Fig. 5) published in 1913. However, the overlap is better seen in more recent publications with colour photomicrographs (Fig. 6).

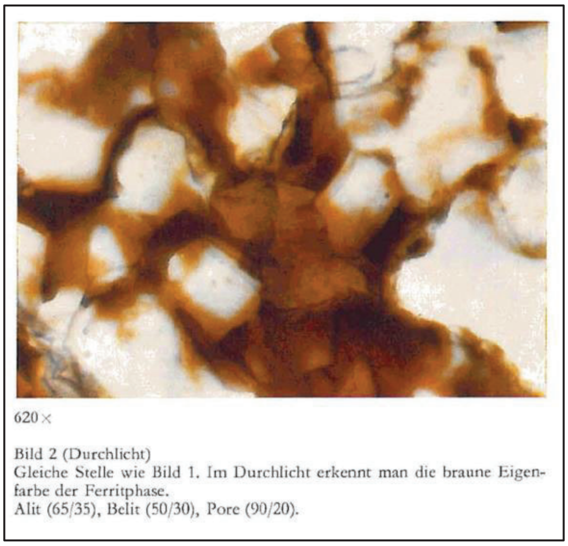

Figure 6 *Photomicrograph of a thin section of shaft kiln clinker; from [12], original width: ca. 100 mm.*

The problem of crystal overlap can be avoided using a microscopic approach originally used by metallographers - reflected or incident light microscopy. Probably the first use is documented in a publication by Ernst Stern from 1908 [13], which includes photomicrographs (Fig. 7) - possibly the first ever published photomicrographs of Portland cement clinker. In the following years, at least two other authors using this method can be found in the literature. These are Cecil Henry Desch (1911, Fig. 8) [14] and Erich Wetzel (1913, Fig. 9) [15]. While Wetzel is cited in more recent literature, e. g. [16], Desch's use of the method seems to have been overlooked later, although the method is described in great detail in his text. In 1935 he published “The Chemistry of Cement and Concrete” together with Sir Frederick Measham Lea [17]. The current 5th edition of this textbook was published by editors Hewlett and Liska in 2019 [18].

Abbildung 6. Erster Angriff von Süßwasser auf Alite

__Figure 7__ Photomicrograph of a polished section of clinker; from [13], original width: ca. 70 mm.

i. Etched with 1 °/₀ HCl. Vertical illumination. × 300 diam.

__Figure 8__ Photomicrograph of a polished section of stationary kiln clinker; from [14], original width: ca. 80 mm.

After 1913 there is a gap of 20 years in the documented use of reflected light clinker microscopy. Only the comprehensive work of B. Tavasci on clinker and cement seems to have initiated a revival. In 1934 Tavasci’s first article with photomicrographs was published [19], many of which were taken of polished sections under reflected light (Fig. 10).

This article was subsequently cited in other influential works in English, e. g. by Insley [20] and Insley and McMurdie [21], which had a multiplier effect on the use of the method, certainly also due to their high-quality photomicrographs (Fig. 11).

5832 V = 200

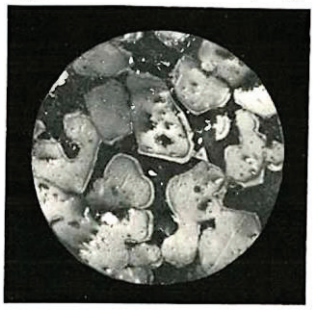

Bild 13. Kleingefüge des Schliffes von Brennprobe 9. V = 200. ½ Std. bei 1600 C° gebrannt.

__Figure 9__ Photomicrograph of a polished section of laboratory clinker; from [15], original width: ca. 100 mm.

Fig.16-Cl.B-R.1-150×-Zona alitica

__Figure 10__ Photomicrograph of a polished section of clinker; from Tavasci 1934 [19], original width: ca. 55 mm.

Tavasci’s paper also addressed the problem of the different clinker phases showing very little contrast in polished sections. It lists the effects of different etchants on the optical properties to allow the differentiation of phases, crystals and sometimes even zonations in crystals. Etching methods had already been discussed by Stern [13]. Many etchants were tried out in the following decades. In 1968, D. B. Ellson and J. H. Weymouth published a short booklet with a large table (about 76 x 54 cm²), listing - in font size 5 - the effects of 43 etchants on 16 different phases that might occur in Portland cement clinker and related materials [22].

FIGURE 4.—*Low-heat clinker, brand A.*

Reflected light. Magnification 500 times. The letter designations on the photomicrograph refer to constituent designations in the text, p. 855.

Figure 11 *Photomicrograph of a polished section of clinker; from [20], original width: ca. 110 mm.*

Today, one or a combination of the following etchants are commonly used: alcoholic nitric acid ("nital"), hydrofluoric acid vapour, acetic acid vapour, aqueous ammonium chloride, alcoholic dimethyl ammonium citrate (DAC) and aqueous potassium hydroxide.

Important monographs

Based on microscopic results as well as other methods, in particular XRD and laboratory experiments, the "constitution" of Portland cement clinker was better understood during the first half of the 20th century. More and more comprehensive works on clinker microscopy were published. Initially, these dealt mainly with the clinker phases and their properties, often including descriptions of preparation and microscopy methods (e. g. [20, 21, 23, 24, 25]) and many photomicrographs.

Over time, however, the focus shifted more and more to microstructural features and their correlation with the production conditions such as raw meal chemistry, mineralogy and fineness, process technology, fuel properties or temperature profiles in different areas of the kiln system. These observations allowed troubleshooting and optimisation of the production process on the one hand, and prediction and optimisation of cement properties on the other.

The increasing knowledge of the relationships between production parameters, clinker properties and cement properties were described in articles and, more importantly, collected in monographs. These monographs were published in the second half of the 20th century by cement industry associations and their research institutes, by cement producers or by suppliers of equipment and services to the cement industry (e. g. [12, 16, 26, 27, 28, 29], Fig. 12).

The most comprehensive work is Campbell's "Microscopical Examination and Interpretation of Portland Cement Clinker" [16], which not only contains a large number of photomicrographs but also references a large number of publications. Ono's work [29] also stands out because it contains many beautiful large photomicrographs (Fig. 13) and describes an approach to microscopic analysis of clinker known as "Ono's method". It can be carried out on powder mounts of ground clinker and focuses on quantifying or categorising just four key clinker properties.

Figure 12 *Covers of monographs on optical clinker microscopy; from top left to bottom right: [12, 28, 26, 16, 29, 27].*

These properties (size and birefringence of alite, size and colour of belite) are related to specific burning conditions in the kiln as well as to the properties of the cement produced with the clinker.

The measurements obtained using Ono's method are, of course, not the only quantifications used in clinker microscopy. In particular, before the introduction of quantitative X-ray diffraction analysis (especially the Rietveld technique) to clinker analysis, point counting on the microscope was the only technique available to quantify the phase contents of clinkers.

Current challenges and future developments

The most pressing issues that clinker microscopy helps to address today and in the future are related to the need to decarbonise the cement industry. Fossil fuels are increasingly being replaced by alternative fuels. Similarly, where possible, natural raw materials are replaced by alternative raw materials from other industrial material streams in which CaO is not bound to CO_2, and, therefore, does not result in CO_2 emissions during the clinker burning process. However, many alternative materials can influence the process and the product properties (e. g. [30]), which need to be understood in order to apply countermeasures or optimise production conditions.

In the future, significant changes in the production technology will occur on the way to carbon-neutral cement production to enable CO_2 capture. Clinker microscopy, among many other analytical methods, will provide important information on how, for example, oxyfuel technology (e. g. [31]), carbonate looping or electrification of process steps influence clinker properties.

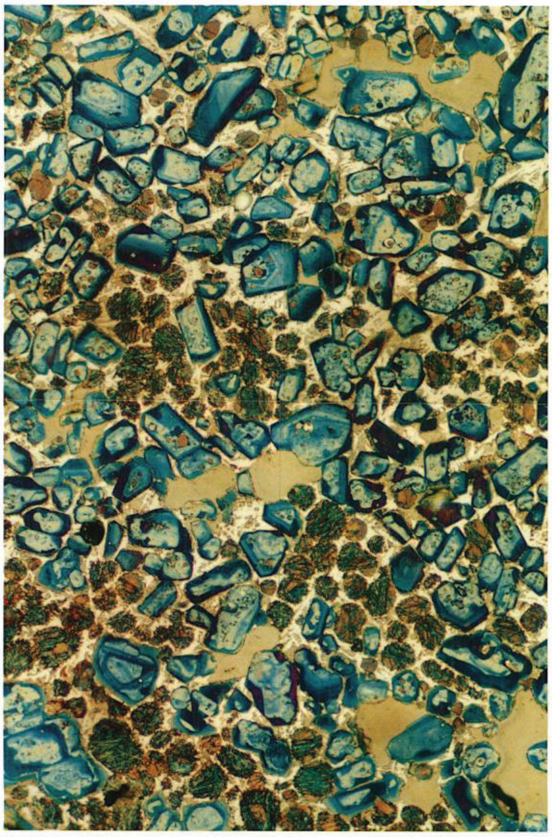

Plate 20. Obj.×20. Plate measures 442×644μm. Well burnt clinker, etched with H_2O 20 sec., 2% NH_4Cl.aq. 5 sec. The etching color changes continuously in many alite crystals. In some alite crystals the change is markedly discontinuous. In some crystals the etching color changes in three or four grades. The zonal structures are not so simple as a composite of two modifications of M1 and M3.

写真 20. 写真寸法 442×644μm (obj×20) 上焼きクリンカー．累帯構造は結晶外形に著しく相似．中心部は強エッチング，明青～白色(d=0.17μm)，外縁部は弱エッチング，濃藍(d=0.09～0.10μm)．中心部強エッチングは数段階に分かれる．最外周部弱エッチング，濃藍は著しく不連続．

Figure 13 *Photomicrograph of a polished section of clinker; from [29], original width: ca. 125 mm.*

The method itself will also continue to evolve. AI-based image analysis will enable new ways of quantifying clinker properties. Together with data from the production process and the quality laboratory, the results of microscopic analyses will be fed into AI applications that will enable process control and quality optimisation with unpreceded speed and precision.

References

[1] Hopfgartner, A.: Analyse zweier hydraulischer Kalke, eines englischen (Portland-Cement) und eines deutschen. Polytechnisches Journal 113, p. 354-357, 1849.

[2] Pettenkofer, M.: Bemerkungen zu Hopfgartner's Analyse eines englischen und eines deutschen hydraulischen Kalkes. Polytechnisches Journal 113, p. 357-371, 1849

[3] Erdmenger, L.: Zur Characteristik der Portlandcementerhärtung – d.) Mikroscopisches über Portlandcement. Thonindustrie-Zeitung 40 (1880), 366-367

[4] Le Chatelier, H.: Recherches expérimentales sur la constitution des ciments et la théorie de leur prise. *Comptes rendus de l'Académie des Sciences* 94, p. 867–869, 1882.

[5] Le Chatelier, H.: Recherches expérimentales sur la constitution des ciments hydrauliques. PhD Thesis, Académie de Paris, 90 pp., 1887.

[6] Thiery, V.: Henry Le Chatelier (1850-1836), the man behind the microscope. Proceedings of the 18th Euroseminar on Microscopy Applied to Building Materials (EMABM), Lille/France, 2022.

[7] Törnebohm, A. E.: Die Petrographie des Portland-Cements. *Thonindustrie-Zeitung* 110, p. 1148-1151 and 111, p. 1157-1159, 1897.

[8] Törnebohm, A. E.: Ueber die Petrographie des Portland-Cements. Verein Skandinavischer Portland-Cement-Fabrikanten, 39 pp., 1897.

[9] Kappen, H.: Das Mineral Belit im Portlandzementklinker. *Mitteilungen aus der Chemisch-Technischen Versuchsstation von Dr. Hermann Passow in Blankenese* 1, p. 22-28, 1904.

[10] Jänecke: Vortrag über die Konstitution des Portland-Cementes. In: Verein Deutscher Portland-Cement-Fabrikanten (ed.): Zur Konstitution des Portland-

Cementes – Vorträge. Cementverlag GmbH, p. 95-122, 1913.
[11] von Glasenapp: Vortrag zur Petrographie des Portland-Cement-Klinkers. In: Verein Deutscher Portland-Cement-Fabrikanten (ed.): Zur Konstitution des Portland-Cementes – Vorträge. Cementverlag GmbH, p. 123-154, 1913.
[12] Gille, F., Dreizler, I., Grade, K., Krämer, H., Woermann, E.: Mikroskopie des Zementklinkers – Bilderatlas. Verein Deutscher Zementwerke e.V. (ed.), Beton-Verlag GmbH, 75 pp., 1965.
[13] Stern, E.: Ueber mikrographische Zementuntersuchung. *Stahl und Eisen* 28 (43), p. 1542-1546, 1908.
[14] Desch, C. H.: The Chemistry and Testing of Cement. Arnold Edward, 267 pp., 1911.
[15] Wetzel, E.: Vortrag über den Stand der auf Antrag des Vereins Deutscher Portland-Cement-Fabrikanten im Königlichen Materialprüfungsamt Berlin-Lichterfelde ausgeführten Arbeiten zur Ermittelung der Konstitution des Portland-Cementes. In: Verein Deutscher Portland-Cement-Fabrikanten (ed.): Zur Konstitution des Portland-Cementes – Vorträge. Cementverlag GmbH, p. 5-29, 1913.
[16] Campbell, D. H.: Microscopical Examination and Interpretation of Portland Cement and Clinker (2nd edition). PCA R&D Serial No. 1754, PCA SP030, Portland Cement Association, 201 pp., 1999.
[17] Lea, F. M., Desch, C. H.: The Chemistry of Cement and Concrete. Longmans, Green & Company, 429 pp., 1935.
[18] Hewlett P. C., Liska, M. (ed.): Lea's Chemistry of Cement and Concrete (5th edition). Elsevier, 858 pp., 2019.
[19] Tavasci, B.: Riserche sulla costituzione del clinker di cemento Portland. *Giornale di chimica industriale ed applicate* 16, p. 538-552, 1934.
[20] Insley, H.: Structural characteristics of some constituents of Portland cement clinker. Research Paper RP917, *Journal of Research of the National Bureau of Standards* 17, p. 353-361, 1936.
[21] Insley, H., McMurdie, H. F.: Minor Constituents in Portland Cement Clinker. Research Paper RP1074, *Journal of Research of the National Bureau of Standards* 20, p. 173-184, 1938.
[22] Ellson, D. B., Weymouth, J. H.: The Etching of Portland Cement Clinker. Chemical Research Laboratories Technical Paper No. 5, Commonwealth Scientific and Industrial Research Organization, Australia, 6 pp., 1968.
[23] Gille, F.: Erkennung der Klinker-bestandteile im durchfallenden und auffallenden Licht. *Zement* 32 (1/2), p. 1-10, 1943.
[24] Alègre, R., Terrier, P.: La microscopie du clinker au Centre d'Etudes des Liants Hydrauliques. *Revue des Matériaux de Construction* 501, p. 165-180, 1957.
[25] Trojer, F.: Phasenaufbau der Portland-zementklinker. Mitteilungen aus dem Forschungsinstitut des Vereins der Österreichischen Zementfabrikanten, Heft 15, 31 pp., 1966.
[26] Hofmänner, F.: Portlandzementklinker – Kleine Gefügekunde. Holderbank Management und Beratung AG (ed.), 50 pp., 1973.
[27] Fundal, E.: Microscopy of cement raw mix and clinker. FLS-review 25, 15 pp., 1979.
[28] Chromý, S.: Portlandsky Cement – Cement Pod Mikroskopem. VHJ Cementarny a vapenky Praha and Vyzkumny ustav stavebnich hmot Brno (ed.), 37 pp.
[29] Ono, Y.: Ono's Method – Fundamental Microscopy of Portland Cement Clinker. Chichibu Onada Cement Corp. (ed.), 229 pp., 1995.
[30] Böhm, M., Pierkes, R., Knöpfelmacher, A., Lipus, K.: Possible effects of aluminium rich particles on the microstructure of Portland cement clinker. Proceedings of the 17th Euroseminar on Microscopy Applied to Building Materials (EMABM), Toronto/Canada, 2019.
[31] Böhm, M., Lindemann Lino, M., Ruppert, J., Hoenig, V.: Impacts of the oxyfuel cooling medium on clinker quality. Proceedings of the 17th Euroseminar on Microscopy Applied to Building Materials (EMABM), Toronto/Canada, 2019.